

[SUBSTITUTE SPECIFICATION-27NOV.1998]

CATALYST TESTING PROCESS AND APPARATUS

X1 PROCESS FOR TESTING CATALYSTS using Thermography

Background of the Invention

for > AD

1. Field of the Invention

The present invention relates to the general field of catalyst testing, generally classified in U. S. Patent Class 502 or 252.

II. Description of the Prior Art

Prior Art will include C & E News, 8 Jan.96, p.30 which teaches reactive plastics, and the many catalyst testing devices and processes known to the petroleum refining art. F.M. Menger, A.V. Fliseev, and V.A. Migulin, "Phosphatase catalysts developed via combinatorial organic chemistry", J. Org. Chem. Vol. 60, pp 6666-6667, 1995. Xiang, 268 Science 1738 and Bricenol, 270 Science 273, both on combinatorial libraries of solid-state compounds; Sullivan, Today's Chem. At Work 14 on combinatorial technology; Nessler 59 J. Org. Chem. 4723 on tagging of combinatorial libraries; Baldwin, 117 J. Amer. Chem. Soc. 5588 on combinatorial libraries.

II. Problems Presented by Prior Art

Catalyst testing is conventionally accomplished in bench scale or larger pilot plants in which the feed is contacted with a catalyst under reaction conditions, generally with effluent products being sampled, often with samples being analyzed and results subjected to data resolution techniques. Such procedures can take a day or more for a single run on a single catalyst. While such techniques will have value in fine-tuning the optimum matrices, pellet shape, etc., the present invention permits the scanning of dozens of catalysts in a single set-up, often in less time than required for a single catalyst to be evaluated by conventional methods. Further, when practiced in its preferred robotic embodiments, the invention can sharply reduce the labor costs per catalyst screened.

Summary of the Invention

General Statement of the Invention

According to the invention, a multisample holder (support) e.g., a honeycomb or plate, or a collection of individual support particles, is treated with solutions/suspensions of catalyst ingredients to fill wells in plates, or to produce cells, spots or pellets, holding each of a variety of combinations of the ingredients, is dried, calcined or otherwise treated as necessary to stabilize the ingredients in the cells, spots or pellets, then is contacted with a potentially reactive feed stream or batch e.g., to catalyze biochemical reactions catalyzed by proteins, cells, enzymes; gas oil, hydrogen plus oxygen, ethylene or other polymerizable monomer, propylene plus oxygen,

or CCl_2F_2 and hydrogen. The reaction occurring in each cell is measured, e.g. by infrared thermography, spectroscopic, electrochemical, photometric, thermal conductivity or other method of detection of products or residual reactants, or by sampling, e.g. by multistreaming through low volume tubing, from the vicinity of each combination, followed by analysis e.g. spectral analysis, chromatography etc, or by observing temperature change in the vicinity of the catalyst e.g. by thermographic techniques, to determine the relative efficacy of the catalysts in each combination. Robotic techniques can be employed in producing the cells, spots, pellets) etc. Each of these parameters is discussed below:

Catalysts: Biotechnology catalysts include proteins, cells, enzymes, etc. Chemical conversion catalysts include most of the elements of the Periodic Table which are solid at the reaction conditions. Hydrocarbon conversion catalysts include Bi, Sn, Sb, Ti, Zr, Pt, the rare earths, and many possible candidates whose potential has not yet been recognized for the specific reaction. Many synergistic combinations will be useful. Supported metals and metal complexes are preferred. The chemical catalysts can be added to the substrate (support) as elements, as organic or inorganic compounds which decompose under the temperature of the stabilizing step, depositing the element or its oxide onto the substrate, or as stable compounds.

Supports: Supports can be inert clays, zeolites, ceramics, carbon,

1 plastics, e.g. reactive plastics, stable, nonreactive metals, or combinations
2 of the foregoing. Their shape can be porous
3 honeycomb penetrated by channels, particles (pellets), or plates onto
4 which patches (spots) of catalyst candidates are deposited or wells in
5 plates. Conventional catalyst matrix materials such as zeolites e.g.
6 zeolite USY, kaolin, alumina, etc. are particularly preferred as they
7 can simulate commercial catalysts.

8
9 **Preparation:** The catalyst candidate precursors can be deposited onto
10 the supports by any convenient technique, preferably by pipette or
11 absorbing stamp (like a rubber stamp), or silk screen. In preferred
12 embodiments, the deposition process will be under robotic control,
13 similar to that used to load multicell plates in biochemical assays.
14 Many of the spots of catalyst will be built up by several separate
15 depositions e.g. a channel penetrating a honeycomb can be plugged
16 at one third of its length and the channel filled with a catalyst
17 solution in its upper third, then the plug can be moved to the two-
18 thirds point in the channel and a second catalyst pipetted in, then the
19 plug can be removed and a third catalyst solution added, resulting in
20 a channel in which reactants contact three catalysts successively as
21 they flow through the channel. Catalyst can also be added by ion
22 exchange, solid deposition, impregnation, or combination of these.
23 The techniques of combinatorial chemical or biological preparation
24
25
26

1 can preferably be utilized to prepare an array of candidate catalysts
2 with the invention. Coprecipitates of two or more catalysts can be
3 slurried, applied to the support, then activated as necessary.

4 Catalysts can be silk screened onto a support plate or inside of a
5 support conduit, and successive screenings can be used to add
6 different catalyst combinations to different spots.

7 **Stabilizing Step:** Once the catalysts are in place on the support, any
8 suitable technique known to the art can be used to stabilize, and/or
9 activate the particular catalysts chosen, so they will remain in place
10 during the reaction step. Calcining, steaming, melting, drying,
11 precipitation and reaction in place will be particularly preferred.

12 **Reactants:** The Invention has utility with any reaction which can be
13 enhanced by the presence of a catalyst, including biological
14 reactions and inorganic and organic chemical reactions. Chemical
15 reactions include polymerization reactions, halogenation, oxidation,
16 hydrolysis, esterification, reduction and any other conventional
17 reaction which can benefit from a catalyst. Hydrocarbon conversion
18 reactions, as used in petroleum refining are an important use of the
19 invention and include reforming, fluid catalytic cracking,
20 hydrogenation, hydrocracking, hydrotreating, hydrodesulfurizing,
21 alkylation and gasoline sweetening.

22 **Sensors:** The sensors used to detect catalytic activity in the
23 candidate catalysts are not narrowly critical but will preferably be as
24 simple as practical. Chromatographs, temperature sensors, and
25 spectrometers will be particularly preferred, especially those adapted
26 to measure temperature and/or products near each specific catalyst

spot e.g. by multistreaming, multitasking, sampling, fiber optics, or laser techniques. Thermography, as by an infrared camera recording the temperature at a number of catalyst sites simultaneously, is particularly preferred. Other suitable sensors include NMR, NIR, TNIR, electrochemical, fluorescence detectors, Raman, flame ionization, thermal conductivity, mass, viscosity and stimulated electron or X-ray emission. Sensors can detect products in a gas or liquid stream or on the surface of the support.

Endothermic reactions exhibit reduced temperature at best catalysts. Some sensors employ an added detection reagent, e.g. ozone to impart chemiluminesce.

Taggants: Optionally taggants (labels) can be added to identify particular catalysts, particularly where particles are employed as supports for the catalysts. These taggants can be conventional as discussed in the literature. Taggants can be chemicals which are stable at reaction conditions or can be radioactive with distinctive emissions. The techniques of combinatorial chemistry will be applicable with taggants as well as with catalysts chosen to suit the particular reaction to be enhanced by the catalyst.

Batch or Continuous: While the invention will be preferred on a flow basis, with reactants flowing by the catalyst spots under reaction conditions, batch testing e.g. in a stirred autoclave or agitated containers, can be employed, particularly in biological reactions.

Temperatures, pressures, space velocities and other reaction

1 **conditions:** These will be determined by the reactants and reaction.
2 Elevated pressures can be provided as reaction conditions by
3 encasing the support in a reaction chamber with a sapphire or
4 similar window for observation by the sensing means, or with
5 pressure-tight leads extending through the reactor walls.
6

7 **II. Utility of the Invention**

8 The present invention is useful in the testing of catalysts for
9 biotechnology, for promotion of gas phase and liquid phase
10 reactions; under batch or, preferably, continuous flowstream
11 conditions; at elevated, reduced or atmospheric pressure; and saves
12 both elapsed time and labor in screening for improved catalysts to
13 promote a desired reaction.
14
15
16

17 **Brief Description of the Drawings**

18 Figure 1 is a schematic diagram of a preferred honeycomb
19 support with a robotic pipetting device depositing different
20 combinations of catalyst ingredients into each of the channels
21 running through the honeycomb, which is thereafter calcined to
22 stabilize the catalysts in each channel.
23

24 Figure 2 is shows schematically the honeycomb of Fig. 1
25 being contacted by reactants flowing through the channels.

26 Figures 3a and 3b are alternative schematic diagrams of one

1 channel of the honeycomb of Fig. 2 with a detector sensing the
2 products exiting the channel by measuring absorption in a laser
3 beam directed through the products or the channel.

4
5 Figure 4a shows a channel plugged at its midpoint prior to
6 receiving a solution of catalyst and Figure 4b shows the plug moved
7 to the end of the channel, so as to form a channel having one
8 catalyst in one half its length and another catalyst in its other half.

9
10 Figure 5 shows schematically a sheet of support onto which 15
11 spots of different catalyst combinations have been deposited, as
12 discussed in example 1.

13
14 Figure 6a shows an array of particles (pellets) of support in
15 place in a reactor after having been ion exchanged with different
16 catalyst combinations on different pellets (denoted schematically by
17 different markings on the pellets in the Figure). Figure 6b shows a
18 packed reactor which is less preferred because upstream pellets see
19 fresh feed, while downstream pellets see partially reacted feed.

Figure 7 shows schematically the use of various detectors on the candidate catalyst array of Figure 5.

Figure 8 shows schematically the use of thermal, electrochemical, flame ionization, etc. detectors on the candidate catalyst array of Figure 5.

Figure 9 shows schematically the use of low volume sampling tubes with various analyzers on the candidate catalyst array of Figure 5.

Figure 10 shows schematically the use of a candidate catalyst array deposited on the interior of a monolith.

Figure 11 shows schematically the use of a flow reactor with sapphire window open to various detectors on the candidate catalyst array of Figure 5, and shows optional pressure tight electrical leads 13 for leading to a detector.

Figure 12 shows schematically the apparatus of Example 13.

Figure 13 shows schematically the apparatus of Examples 14 and 16.

Description of the Preferred Embodiments

Example 1

Referring to Figure 1, a sheet of alpha alumina **10** is wash-coated with particles of porous gamma-alumina by standard methods. Solutions of oxalate salts of 12 different transition metal elements are prepared in the wells of a 24 well microtiter dish made of polystyrene. A Beckman Biomek 2000 robotic automated liquid handling system is used to prepare dilutions and mixtures from the original stocks, again in the wells of microtiter style plates. The robot is used to deposit 20 microtiter aliquots of each of the resulting solutions at defined positions (spots) **12** on the surface of the alumina support **10**, which is then dried, calcined and inserted into a reactor capable of temperature control at temperatures from 100 to 350 degrees centigrade. After reduction, a potentially reactive mixture of oxygen and hydrogen is fed to the reactor. An Agema infra-red sensitive camera **14** is used to observe the alumina support through infra-red-transparent sapphire windows **16** shown in Figure 11, via a polished metal mirror. The camera is set so that the lower end of its dynamic range corresponds to a temperature of about 40 degrees C. below the feed temperature and the maximum signal is associated with a temperature about 200 degrees higher. Compositions catalyzing the reaction are revealed by the localized temperature increases (decreases for endothermic reactions) around spots **12** of

that composition, as shown on photograph 18 in Figure 5.

Example 1a

Catalysts are alternatively identified by conducting the reaction in the presence of strong ultraviolet and/or visible light illumination. with infrared thermography being conducted immediately after the illumination is turned off, or through the use of a short pass filter on the illumination source to eliminate contaminating infra-red radiation.

Example 2

Referring to Figure 2, a porous alumina monolith 20 (Corning) having square or circular cross-section channels extending in a regular array through its entire thickness is treated in each channel with a solution of catalyst precursors of differing compositions, with each composition being segregated in its own channel. After drying, calcination, etc., the activated monolith is placed in contact with a flowing potentially reactive mixture at an elevated temperature, and observed in the infra-red using an Agema model camera. The enthalpy of reaction produces localized temperature differences in the vicinity of compositions exhibiting catalytic activity and these are observed as temperature variations near the exits of the channels.

Example 3

Referring to Figure 3, a porous ceramic monolith 20 of the type described in Example 2, bearing various catalyst compositions in its channels is installed in a reactor (not shown) in such a way that the entire length of each channel can be observed through sapphire windows at the ends of the reactor. A broad-spectrum thermal infrared source is installed at one end of the reactor, giving an areal infrared energy flux density. An Agema IR-sensitive camera is positioned in such a way as to observe the infra-red source directly through a significant fraction of the pores. An interferometric or other filter is installed on one side of the reactor between the camera and the infra-red source such that the light reaching the camera from the source is substantially limited to wavelengths between 4 and 4.5 microns. Observation of absorbency at this wavelength range is used to compare candidate catalyst compositions on the basis of their production of carbon dioxide, an undesired side product of the intended reaction. Catalyst compositions chosen for low carbon dioxide formation (in combination with high overall conversion activity as measured by infra-red absorbance of the desired product or by infrared thermography) are found to have high selectivity for the desired product over the carbon dioxide side product.

Example 4.

A collection of catalyst precursor compositions is produced by automated liquid handling device, and a catalyst support particle is contacted with each composition. After further treatment to

1 stabilize and activate the catalyst precursors, catalyst pellets are
2 arrayed on a surface, exposed to a potentially reactive environment
3 and their activity determined by infrared thermography.
4

5 **Example 5.**

6 Solutions of combinations of catalyst precursors are prepared in a
7 variety of separate vessels. Each composition also contains a small
8 quantity of a labeling material (e.g., stable isotopes of the element
9 carbon or sulfur in varying ratios). Catalyst support particles are
10 contacted with catalyst precursor preparations, and activated.
11 Pellets are then contacted one at a time with a potentially reactive
12 mixture (for example, by elutriation into an enclosed volume) and
13 their activity measured (by thermography, by spectroscopic
14 measurement of products, or sampling of the surrounding vapor or
15 liquid phase). Particles showing activity are collected and
16 individually analyzed for their content of the labeling material so as
17 to determine the composition giving the desired catalytic activity.
18
19

20 **Example 6.**

21 Example 2 is repeated except that only a portion of the pore length
22 is coated with a catalyst candidate so as to allow for observation of
23 unmodified monolith pore wall as a control reference standard for
24 optical uniformity.
25

26 **Example 7.**

1
2 The emissivity of the support monolith pores of the support 20 of
3 Example 2 is mapped at a wavelength of interest by holding the
4 monolith at the intended experimental temperature in
5 reactants. Digitally stored maps of the emissivity are used to
6 normalize the infra-red energy flux measured under experimental
7 conditions, to improve the accuracy with which local temperatures
8 can be estimated.

9 10 **Example 8.**

11
12 A surface of high, substantially uniform emissivity is located at the
13 end of the monolith of Example 2, away from the camera, in close
14 radiative heat transfer/contact with the monolith channel material.
15 The temperature of the portion of the surface closest to the open end
16 of each channel is observed. In this case, it is necessary that gas be
17 admitted into the channels past the uniform radiative surface, either
18 by means of pores or by means of a small offset between the
19 radiative surface and the monolith.

20 21 **Example 9.**

22
23 Alternatively, spots of catalysts can be deposited on the inner
24 surface of a reactor e.g. a tube formed of the support material as shown in
25 Figure 10, and temperature of the corresponding spots on the outside of
26 the reactor can be measured to determine by conduction whether the

respective catalyst has increased or decreased in temperature under the reaction.

Example 10.

The process of Example 1 is repeated except that the reactants are in the liquid phase and a liquid phase assay is used (Figure 12) to detect the activity of individual catalyst candidates.

Example 11.

The experiment of Example 4 is repeated except that the metal loading is directly measured by dissolving the pellet and directly analyzing the metal loading.

Example 12.

A sheet of alpha alumina **5** in Figure **12**, is wash coated with particles of porous gamma-alumina by standard methods. Solutions of oxalate salts of 12 different transition metal elements are prepared in the wells of a 24 well micro titer dish made of polystyrene. A Beckman Biomek 2000 automated liquid handling system is used to prepare dilutions and mixtures of the original stocks, again in the wells of microtiter style plates. The Biomek robot **6** is used to deposit 40 microliter aliquots of each of the resulting solutions at defined positions on the surface of the alumina support, which is then dried, calcined and

1 inserted into a reactor (as shown in Figure 11) controlled at a temperature
2 of 200 degrees centigrade. A gaseous mixture of hydrogen (97.5%) and
3 oxygen (2.5%) is fed at a temperature of 200 degrees centigrade. Using
4 the apparatus of Figure 11, an infra-red sensitive camera 14 is used to
5 observe the alumina support through infra-red-transparent sapphire
6 windows 16. The camera is set so that its lower range corresponds to the
7 feed temperature and the maximum signal is associated with a
8 temperature degrees 20 degrees higher. Compositions catalyzing the
9 reaction are revealed by the localized temperature increases around spots
10 of that composition.
11
12

Example 13.

13
14 A porous alumina monolith 140 in Figure 12, having square pores
15 extending in a regular array through its entire thickness at a density of 25
16 per square inch is washcoated with alumina particles. The channels are
17 then partially filled with solutions of differing compositions, each
18 containing one or more metal oxalate or nitrate salts, with each
19 composition being segregated in its own channel or set of channels.
20 After drying and activation in the presence of hydrogen gas, the
21 activated monolith is placed into a sapphire-window-equipped
22 reactor 150 in which it can be observed in the infrared using an IR-
23 sensitive camera 145. The camera is positioned in such a way as to
24 observe the walls of the support. The relative emissivity of the
25 support at each pixel is determined by imaging the monolith in the
26 IR while holding the reactor and monolith at each of several

constant temperatures while flowing nitrogen gas **153** through the reactor.

The reactor is then fed with a gas mixture of 2.5 mole % oxygen in hydrogen **154**. The reactor and feed temperatures are originally set to 40 degrees centigrade, and are gradually increased While the catalyst-bearing monolith is repeatedly imaged in the IR. The temperature in each cell may be judged by observing the cell at a position adjacent to the end of the catalyst-precursor-coated section of the channel, or by normalizing the observed IR energy emission by the emissivity calculated from the images taken under nonreactive conditions. The compositions in the cells showing the earliest temperature increase above the reactor temperature are useful as hydrogen oxidation catalysts.

Example 14.

A porous alumina monolith **140** in Figure **13** having square channels in a regular array extending through its entire 10 centimeter thickness at a density of 25 per square inch is washcoated with alumina particles. The channels are then partially filled with solutions of differing compositions, each containing one or more metal salts and in some cases also candidate modifiers such as barium, cesium or potassium compounds, each composition being segregated in its own channel or set of channels.

After drying and reduction in the presence of hydrogen gas, the

1 activated monolith is placed into a reactor in which it can be
2 observed through a sapphire window 172 using an IR-sensitive camera
3 170.

4 This first window 172 is positioned 0.5 centimeter from the surface of
5 the monolith. The camera 170 is positioned in such a way as to look
6 through the window 172, through the channels of the support and
7 through a second sapphire window 174 toward a source of IR radiation
8 164.

9 The reactor 168 is then fed with methane gas, mixed with oxygen
10 and argon, in such a way that the gas 165 flows through the channels of
11 the monolith toward the camera. An optical filter 162 which selectively
12 passes IR radiation at 4.3 microns, a wavelength which is strongly
13 absorbed by carbon dioxide, is inserted between the IR source and
14 the camera. The effective concentration of carbon dioxide in each
15 channel is inferred from the IR intensity at 4.3 microns seen in that
16 channel. The reading at 4.3 microns for each pixel is divided by the
17 reading taken through a filter selective for an IR wavelength which
18 is near 4.3 microns, but which is not absorbed strongly by carbon
19 dioxide, methane or water, to compensate for potential optical
20 artifacts.

21
22 Compositions giving high concentrations of carbon dioxide
23 after long exposures to operating conditions are useful in catalytic
24 oxidation of methane.
25
26

Example 15.

Solutions of combinations of catalyst precursors are prepared in a variety of separate vessels. Each composition also contains a small quantity of a labeling material (e.g., stable isotopes of the element sulfur in varying ratios unique to each composition). Catalyst support particles are contacted with the preparations of catalyst precursor compositions, and activated. Pellets are then contacted one at a time with a potentially reactive mixture (for example, by elutriation into an enclosed volume) and their activity measured (by thermography, by spectroscopic measurement of products, or sampling of the surrounding vapor or liquid phase). Particles showing activity are collected and individually analyzed for their content of the labeling material so as to determine the composition giving the desired catalytic activity.

Example 16.

A Teflon block monolith **140** in Figure **13**, having square channels in a regular array extending through its entire thickness at a density of 9 per square inch is prepared in such a way that a shallow well exists at the bottom of each channel. Each well is charged with a different polymer preparation bearing sulfonic acid groups on its surface, and a porous retaining mesh installed to keep the polymer samples in place.

The catalyst-charged monolith is placed into a reactor in which it can be observed through a window **172**, positioned 0.5 centimeter from

1 the surface of the block. A camera 170 is positioned in such a way as to
2 look via through the sapphire window, through the channels of the
3 support and through a second window 174, toward a source of polarized
4 light 164. A polarizer 162 is installed between the block and the camera.

5 A sucrose solution 166 is fed to the reactor in such a way as to flow
6 through the channels of the block. The angle of rotation of polarized
7 light in passing through the liquid in each channel is measured by
8 rotating the polarizer to various angles, and observing the variation
9 in brightness of the light passing through each channel. The
10 candidate catalysts found in channels giving the greatest change in
11 the angle of rotation are useful as catalysts of sucrose hydrolysis.

13 **Example 17.**

14 Catalysts for photooxidation of hexane are identified by conducting
15 the reaction in the apparatus of Example 16 in the presence of
16 strong ultraviolet and/or visible light illumination, with infra-red
17 thermography being conducted immediately after the illumination is
18 turned off, or through the use of a short pass filter on the
19 illumination source to eliminate contaminating infrared radiation.

21 **Example 18.**

22
23 Samples of cyanogen bromide-activated cross linked agarose
24 beads are exposed to solutions of alcohol oxidase at varied pHs, salt
25 concentrations, and enzyme concentrations. After coupling of the
26 enzyme, residual active groups are quenched with ethanolamine, the

beads are washed, and each sample placed in a separate well of a multiwell plate. The plate is exposed to a flowing air stream containing ethanol vapor and observed with an Amber infrared-sensitive camera.

The samples showing the greatest temperature increase are selected as highly active immobilized alcohol oxidase catalysts.

Example 19.

Samples of cyanogen bromide activated cross linked agarose beads are exposed to solutions of anti-alcohol oxidase antibodies at varied pHs, salt concentrations, and antibody concentrations.

After coupling of the enzyme, residual active groups are quenched with ethanolamine. The beads are washed, exposed to a solution of alcohol oxidase) washed again, and each sample placed in a separate well of a multiwell plate. The plate is exposed to a flowing air stream containing ethanol vapor and observed with an Amber infrared-sensitive camera.

The samples showing the greatest temperature increase are selected as highly active immobilized alcohol oxidase catalysts.

Example 20

A ceramic monolith having channels arranged in perpendicular row/column format passing through its entire thickness is washcoated with porous alumina particles and all the channels in each column are

1 treated with the same catalyst precursors, which are activated. A
2 potentially-reactive stream is flowed through the channels of the monolith,
3 and a multiwavelength beam of radiation is passed over the surface of the
4 monolith, parallel to each column, to a detector situated at the end of the
5 column. The composition of the stream leaving the pores in that
6 column is estimated by processing the detector output, including
7 Fourier transformation and/or weighted summation/differencing of
8 the intensities at different wavelengths.

10 **Example 21.**

11 Pellets bearing catalytically-active groups capable of catalyzing the
12 conversion of both the D- and L- stereoisomers of a reactant are
13 treated with a variety of substances potentially capable of
14 preferentially suppressing (temporarily or permanently) the
15 conversion of the L-stereoisomer of that compound by that catalyst.
16 The pellets are distributed among the wells of a multiwell plate
17 and exposed to a mixture of the isomers of the compound to be
18 modified. Pellets treated with the suppressor giving the greatest
19 reduction in the activity for conversion of the L-isomer are useful in
20 stereoselective modification of the D-isomer.

22 **Example 22.**

23
24 A ceramic monolith having channels arranged in perpendicular
25 row/column format passing through its entire thickness is
26 washcoated with porous alumina particles and the channels treated

1 with catalyst precursors, which are activated. A potentially-reactive
2 stream is flowed through the channels of the monolith. A manifold
3 consisting of an array of tubes, each smaller than the dimensions
4 of an individual channel, is used to introduce a stream containing
5 ozone into the stream flowing through each channel, near its outlet.
6 Reaction of the introduced ozone with the desired product
7 liberates light, which is detected by a camera directed at the
8 monolith. The catalyst composition giving the strongest light output
9 is a useful catalyst for conversion of the reactants to the ozone-
10 reactive desired product.

13 **Example 23.**

14 A ceramic monolith having channels arranged in perpendicular
15 row/column format passing through its entire thickness is
16 washcoated with porous alumina particles and the channels treated
17 with catalyst precursors, which are activated and then exposed to a
18 potentially deactivating substance. A potentially-reactive stream is
19 flowed through the channels of the monolith. A manifold consisting
20 of an array of tubes, each smaller than the dimensions of an
21 individual channel 71 is used to sample the stream flowing within
22 each channel. Samples from each channel in turn are introduced
23 into a gas chromatograph-mass spectrometer combination through
24 an arrangement of switching valves, and catalyst compositions
25 giving the highest yield of desired products are useful in conversion
26

1 of that reactive stream.

3 **Modifications**

4 Specific compositions, methods, or embodiments discussed
5 are intended to be only illustrative of the invention disclosed by this
6 specification. Variations on these compositions, methods, or
7 embodiments are readily apparent to a person of skill in the art
8 based upon the teachings of this specification and are therefore
9 intended to be included as part of the inventions disclosed herein.
10 For example, statistically-designed experiments, and automated,
11 iterative experimental process methods can be employed to obtain
12 further reductions in time for testing. Attachment/arraying of
13 preformed catalytic elements (especially precipitates, also single
14 molecules and complexes such as metallocenes) onto a support,
15 preferably by precipitating or deposition is useful in many cases.

16
17 Detection can involve addition of some reagent to the stream leaving
18 each candidate, the reagent allowing detection of a catalyst product
19 through staining or reaction to give a detectable product, light, etc.

20
21 The supports can comprise arrays with special arrangements for
22 e.g., a header of multiple delivery tubes for uniform flow distribution,
23 inserted into each channel in a block.

24
25 The detection means can comprise electrochemical means, or a
26 gamma camera for metals accumulation measurement, imaging

1 elemental analysis by neutron activation and imaging by film or
2 storage plate of emitted radioactivity, temperature measurement by
3 acoustic pyrometry, bolometry, electrochemical detection.
4 conductivity detection, liquid phase assay, preferably dissolving the
5 support pellet and directly analyzing the metal loading; measuring
6 refractive index in the liquid phase; observing the IR emissions of
7 product gases directly, without the usual source and using instead
8 the radiation hot gases emit at characteristic wavelengths.

9 Other modifications can include testing for selectivity after
10 deliberately poisoning some sites, especially in chiral catalysis, etc.

11 The formulations can be supported in the form of spots or layers on
12 the surface of a support containing wells or channels or channels
13 extending across the entire extent of the support. The support can
14 comprise a form of carbon, zeolite and/or plastic. The plastic can
15 comprise a reactant. The support can hold a form of catalyst made
16 by coprecipitation, or aluminum, or particles.

17 At least one of the formulations can preferably comprise a material
18 selected from the group consisting of transition metals, platinum,
19 iron, rhodium manganese, metallocenes, zinc, copper, potassium
20 chloride, calcium, zinc, molybdenum, silver, tungsten, cobalt and
21 mixtures of the foregoing.

22 The label can comprise different isotopes or different mixtures of
23 isotopes.

24 The reaction conditions can comprise a pressure greater than one
25 bar absolute pressure and the contact can be at a temperature
26 greater than 100 degrees centigrade

1 The method can comprise detection of temperature changes in the
2 vicinity of a respective formulation due to reaction endotherm or
3 exotherm.

4 The method can comprise treatment with a reducing agent.

5 The contacting step can be carried out in the presence of compounds
6 which modify the distribution of the metal within the porous
7 support.

8 The candidate catalyst formulations can be contacted in the form of
9 spots or layers on the surface of a support containing a washcoat
10 supported by an underlayer.

11 The stabilizing step can be carried out with a temperature gradient
12 or other means whereby certain candidate catalyst formulations are
13 exposed to different temperatures. The stabilizing can comprise
14 calcining, steaming, drying, reaction, ion exchange and/or
15 precipitation.

16 The detection of temperature changes due to reaction can employ a
17 correction for emissivity variations associated with differences in
18 chemical composition.

19 The array of formulations to be tested can comprise preformed
20 metallocenes or other catalytic complexes fixed to a support.

21
22 The infrared radiation can be detected through the use of
23 nondispersive infrared spectroscopy, or infrared-
24 sensitive photographic film. The detector means can comprise
25 means for physically scanning over an array of candidate
26 formulations.

1 Observations at multiple wavelengths can be processed by
2 mathematical manipulation e.g. transformation, weighted
3 summation and/or subtraction, etc.

4 Reaction activity, reactants, or products can be detected through the
5 use of an added reaction which signals the presence of reaction or
6 particular compounds or classes of compounds.

7 Chemiluminescence can be used as an indicator of reaction activity,
8 or particular compounds or classes of compounds.

9 A substantially collimated radiation source can be employed
10 in product detection/imaging.

11 Multi-tube sampling can be used to lead into a mass spectrometer,
12 chromatograph, or optical monitor.

13 To simulate aging, etc., the formulations can exposed to a
14 deleterious agent which reduces the activity of at least one
15 formulation by at least 10%, and then optionally exposed to steam,
16 heat, H₂, air, liquid water or other different substance(s) or
17 condition(s) which increase the activity of at least one member of
18 the collection by at least 10% over its previously-reduced activity
19 whereby regenerability, reactivatability, decoking, or other catalyst
20 property is measured. The deleterious agent can comprise elevated
21 temperature, V, Pb, Ni, As, Sb, Sn, Hg, Fe, S or other metals, H₂S,
22 chlorine, oxygen, Cl, and/or carbon monoxide.

23
24 Reference to documents made in the specification is intended to
25 result in such patents or literature being expressly incorporated
26 herein by reference.